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Pigment analysis by Raman microscopy and portable X-ray fluorescence (pXRF) of 13th-14th century illuminations and cuttings from Bologna

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Abstract

Non-destructive pigment analysis by Raman microscopy and portable X-ray fluorescence (pXRF) has been carried out on some Bolognese illuminations and cuttings chosen to represent the beginnings, evolution and height of Bolognese illuminated manuscript production. Dating to the 13th and 14th centuries and held in a private collection, the study provides evidence for the pigments generally used in this period. The results, which are compared with those obtained for other north Italian artwork, show the developments in usage of artistic materials and technique. Also addressed in this study is an examination of the respective roles of Raman microscopy and pXRF analysis in this area of technical art history.

Keywords: Raman microscopy, pigments, portable X-ray fluorescence, illuminated manuscripts and cuttings, Bologna

Introduction

Technical art history studies of illuminated manuscripts and cuttings ranging in date from the Anglo-Saxon period (8th C) to late medieval times are numerous. This situation owes much to the role of Raman microscopy (RM) which has been notably successful in achieving high-resolution identifications of pigments. As a result, the evolution of developments in artistic materials from the Roman period onwards is becoming better understood. The Roman palette used in wall paintings was dominated by locally available minerals, earths and plant extracts with a limited range of synthetic materials such as lead white, verdigris, red lead and Egyptian Blue [1,2,3]. It was later supplemented by other pigments as painting media and techniques diversified in the Byzantine and neighbouring worlds. One such pigment was lazurite (extracted from lapis lazuli found in Afghanistan) which was identified as a blue pigment in the earliest (i.e. 10^{th} to 13^{th} C) Armenian and Byzantine manuscripts reviewed by Orna [4]. By the 14^{th} C, if not earlier, communications by land or sea had enabled painters working in many parts of Europe to access a wide variety of pigments. Besides technical treatises, expertise was probably passed on orally and through practical experience [5]. But underlying the basic commonality of the palette at that time was the way that individual artists could improvise or experiment, according to the status or scale of the manuscript (ms), by mixing colours that were already part of that palette. One of the issues considered in this paper is the *variability* in artistic materials achieved through improvisation or experiment at the local, *intra*-school level and within a well-defined period.

In the earlier 'Middle Ages' most books were produced in monasteries and other major church establishments [6]. The first RM study of an Anglo-Saxon manuscript was made on the Lindisfarne Gospels which revealed (contrary to perceived wisdom of the day) no trace of lazurite on the manuscript; the blue colour was achieved solely by the use of indigo extracted from the woad plant indigenous in north-east England and Scotland [7]. By contrast and dating a century later (c. 800 AD), the painters of the Book of Kells in Ireland made the same use of indigo but employed lazurite as well [8]. Differential access to lazurite was surely an issue at the time as this pigment was not found on any of the other 8th, 9th and 10th C manuscripts studied in the British Library [9] until it was identified as a c. 920 AD pigmentary addition made as part of the restoration of a much earlier ms [10].

With the growth of cities and the evolution of the 'Gothic' styles from the 'Romanesque' between 1100 and 1200, professional resident bookmakers and mendicant clergy took over from monks. Notable sites were the universities of Paris and Bologna, and later University cities. One of the earliest manuscript studies by RM was of a 13th C Paris bible, in which the following pigments were identified: azurite, orpiment, lazurite, realgar, lead white, red lead, malachite and vermilion [11]. A second early study was of the Skard manuscript, a finely illuminated 14^{th} C Icelandic manuscript (c. 1360). The pigments identified were vermilion, orpiment, realgar, red ochre, azurite, bone white, verdigris, and possibly green earth [12]. Notable was the absence of lead-containing pigments, but whether this was due to stylistic preferences or non-availability of lead pigments in Iceland is not known.

We report here the results of a programme of non-destructive analysis of five illuminations and cuttings of the Bologna school in northern Italy using RM and portable X-ray fluorescence (pXRF). They were chosen to represent the beginnings, evolution and height of Bolognese illuminated manuscript production from examples in a private collection readily available for such analysis; they date to the 13^{th} C and 14^{th} C and provide at least a partial indication of the pigments generally used in this period, though those used in many legal and other academic manuscripts are under-represented, as are the finest pigments of the most luxurious Bolognese productions from the Paleologan Renaissance 'Second Style'. They represent an extended period in which the university city became probably the most productive centre of illumination in Italy incorporating or influencing most artistic trends current in Central and Northern Italy between Naples and Venice. The pigments used are broadly typical of this area, though individual artists and local productions may occasionally make use of distinctive colours perhaps arising from unusual sources of supply. The first four Bolognese cuttings represent the evolution of a descriptive pictorial style in which French Gothic techniques fuse with Romanesque formalism; an increasing illusionism inspired by Byzantine models was rapidly replaced by a new synthesis of Roman and Gothic traditions, commonly but often inaccurately associated with the work of Italian artist Giotto (1266-1337). The fifth fragment represents Bolognese art of perhaps two full stages later, after the generation represented by the immediate followers of the 1328 Master and the Urb. Lat 163 artist, the Illustratore (Tomaso Galvani?) and the 1346 Master, and the arrival of Niccolò da Bologna, the most prolific and perhaps the most distinguished of all Bolognese illuminators, who dominated Bolognese illumination in the second half of the century [13].[1] By the time of Niccolò da Bologna the 'Giottesque' transformation of art was fully realised in Bologna, and new concerns for emotional emphasis and descriptive detail were becoming dominant.

The results are discussed within the context of data obtained from other investigations for comparable productions in northern Italy and beyond. While this study is primarily an investigation in technical art history it also has a methodological aim which is to demonstrate further the combined use of different non-destructive analytical methods for illuminated manuscript analysis which is an established practice in the field [14-17]. Well established though pXRF is in providing the elemental characterization of pigments, it may be insufficient for analysing small areas or those areas containing light elements as found by Jones [18] in his study of illuminated manuscripts held in the University of Glasgow Library's collection [19]. They included: manuscript **(MS) 6** (S.1.6) Bartolo de Sassoferrato, *Treatise on Infortiatum* Bologna (c. 1400); **MS 370 (V.1.7)** Titus, *Livius Patavinus*, Livy *History Bks XXI-XXX* folio 153 Milan (*c*. 1450); **MS 374** (V.1.11) Boethius, *On the consolation of philosophy* ?NE Italy, Genoa (1375); **MS 425** (V.4.9) Lucius Lactantius Bologna (mid-15th C); and **MS General 1060** Michele da Genova (c. 1490; 11,12). The outcome of the present study, in which these

1 Since most medieval illuminators are anonymous it is customary to identify them by reference to their best known or most useful work. In the case of Bolognese artists, two of the most important can be related to dated statutes.

limitations of pXRF have been circumvented using RM in tandem, can now be used to direct further analysis of medieval and Renaissance illuminated manuscripts.

Description of the fragments studied (Figs. 1-5)

1. *Leviticus-Numbers bible* (Fig. 1) – detached leaf from a bible not otherwise known representing the so-called Bolognese 'First Style' (or Academic Style) in a palette and technique generally characteristic of university manuscripts of c 1250-80, probably from relatively early in this period. It is a larger format than usual for the small portable bibles typical of Parisian and Bolognese production generally for mendicants to use in their studies and preaching; however, it is smaller and much simpler in decoration and illustration than the large bibles often commissioned by senior clerics for their own use or for religious houses with which they were associated. In this respect it is more representative of contemporary legal and arts texts which frequently present a similar palette, though usually in less brilliant colours. The style is distinctive, showing a stronger influence of French Gothic on the drawing of the faces than usual in Bologna, but the composition, foliate decoration and calligraphy are entirely typical of Bologna. It presents red and blue book page headers, VI, NV (Leviticus/Numbers), a blue chapter initial and marginal number with red full column and bas-de-page-high filigree enrichment, a rubricated explicit/incipit for Leviticus/Numbers with an excised instruction, and a historiated initial of Moses, horned, addressed by God and standing on a fish, framed by an aedicule and upper castellated compartment.

2. *Tondo* (Fig. 2) - cutting from the bas-de-page of a manuscript, probably but not necessarily liturgical but of substantial size, and painted by the so-called 'Seneca Master' (or First Master of the S. Domenico Choirbooks) active on the choirbooks of the principal house of the Dominicans in Bologna in the early years of the 14th C. The youthful figure holding a scroll suggests St. John the Evangelist, but the absence of either a halo or any evangelical attribute would suggest a prophet or simply a generic figure. The artistic idiom represents a drastic simplification of the 'Second/Paleologan Style' under the influence of Giotto, probably through contact with his work in Padua where Bolognese illuminators also worked. The predominantly blue/lavender/grey/pink/red palette reflects the former along with the rounding of faces, but the simplicity of treatment both in the even tones of the garments and the schematicization of facial features probably reflects the Giottesque style, though less clearly than in the Second Master (B18 Master)'s work, which is very similar. The two artists have a dominant role in the production of Bolognese manuscripts of medium-to-modest quality in the first third of the Trecento (14th C).

3. Initial ‘M’ (large; Fig. 3) - cut from a choirbook to include the crowning petal which was possibly part of a more elaborate foliate flourish surrounding it in the original manuscript: this asymmetrical placing is unusual. This should be similar in character to the previous fragment, though different in function within the book, constituting the initial of an antiphon at a significant point in the manuscript’s liturgical cycle.

4. St. John Baptist cutting (Fig. 4) - illuminated by the First master of Urb lat. 163 (*Digestum Novum*) one of numerous distinct illuminators who collaborated on a considerable number of Bolognese legal manuscripts between 1300 and c. 1330. The combination of a full green and a deep scarlet red is characteristic, and the pale pink reappears in a lighter or more faded version along with a typical blue background lined at the borders with white filigree, as in the previous cutting. The face allows for comparison with the rather more minimal treatment in the second item: its slightly scowling expression with strongly marked horizontals in brows, lips and chin is typical of the artist, along with shallow forehead and heavy beard/hair treatment. In the artist’s more complex scenes the figures are set in structures presenting a strong usually frontal space involving complex structures of both Byzantinising and Roman or Giottesque inspiration.

5. St. James fragment (Fig. 5) - a cutting reduced to a figured detail showing the saint presenting a member of a confraternity or a prospective pilgrim to a lost text or representation of Christ or the Madonna or similar subject of exalted reverence. The prominent staff in James’s hand and the preeminence of the Santiago pilgrimage for the Bolognese suggest that this is the specific context for the original document. This is an early to mid-period work of Niccolò da Bologna, c 1360. Although the Augustinian house in Bologna was dedicated to St. James, and Niccolò illuminated its surviving choirbooks, these were executed in a later phase of his style and are artistically very different. The pigment analysis, however, is perhaps indicative of much of the best Bolognese work of the mid to late 14th C, except that the figures as cropped have no background.

Experimental

RM

The Raman spectroscopic systems used for the present investigation are a Renishaw System 1000 Raman spectrometer (laser wavelength of 632.8 nm), and a Renishaw InVia Raman spectrometer (laser wavelength of 514.5 nm). Each was attached to a Leica microscope and equipped with an 1800 lines/mm grating, a holographic notch filter, a thermoelectrically cooled charge coupled device (CCD) detector operating at a temperature of –70 ºC. Spectra were recorded in the range

2500–100 cm^{-1} by collecting 10–30 accumulations each with a duration of 10 s and an estimated spectral resolution of 1 cm^{-1}; spectra were calibrated using the 520.5 cm^{-1} band of a silicon wafer and compared with those reported in published libraries of spectra obtained from reference materials [2,20-23].

pXRF

Non-destructive elemental analysis was carried out with a Thermo Niton XL3t 900 SHE GOLDD Alloy Analyser, with a 50 kV Ag X-ray tube. The instrument, which was attached to a stand, had a video camera within the analyser head allowing the analysis area (8 mm diameter) on the manuscript to be defined. As wide a range of differently coloured areas as possible was selected for analysis with the proviso that the analysis spots were sufficiently large to encompass fully the diameter of the X-ray beam. Analysis time was 70 s. Niton's TestAllGeo and Mining calibration modes yielded semi-quantitative determinations of the content of thirty elements, of which Ca, Cu, Fe, Pb, Hg, Sn, Au, Si and S appeared to be the most informative in terms of determining the likely identity of the pigment under analysis. It is noted, however, that recent work has shown that two-dimensional scans by macro(MA)-XRF may give superior results [24] in this respect than the single point analyses presented in this study. In the case of manuscripts **1**, **2** and **5** a helium flow through the analyser head helped to improve detection of the light elements present, but an instrument upgrade in advance of analysis of the other two manuscripts obviated its use. In the tables that follow, the element(s) in greatest concentration appear in bold.

Results and Discussion

The results obtained for each manuscript/cutting are shown in Tables 1-5 and Figures 6 & 7 and can be summarised as follows. Vermilion (mercury sulfide) has been used as the red in all fragments (Fig. 6a) and mixed with lead carbonate hydroxide ('lead white') to provide a fleshtone, as in Fragments 2 and 5. Lead white consistently was used for white (Fig. 6b). Orange-red is depicted in the form of lead(II,IV) oxide ('red lead') in one example only (Fragment 1, sites 3-5; Fig. 6c). Yellow is also uncommon: there is a single example of mosaic gold (tin sulfide) used for this colour in Fragment 2 (site 15; Fig 6d) and yellow ochre in Fragment 1 (site 7; Fig. 6e). Certainly, the use of mosaic gold is not uncommon in manuscript illumination [25]. The yellow-brown in Fragment 3 is uncertainly identified; it has a calcium carbonate (chalk) base (site 5; Fig. 6f) which may simply be the gesso layer which may, according to Cennini [26] also contain lead white; indeed XRF frequently detected lead together with calcium in this layer.

There is sophistication in the use of green in two fragments: Fragment 4 features in effect three separate pigment mixtures, one of which contains an organic (indigo; Fig. 7a); the dark green appears to be composed of azurite (Fig. 7b) mixed with yellow iron oxide. Yellow iron oxide (cf. Fig. 6e) was also identified as a component in the green in Fragment 2. In Fragment 3, the green paint used for the leaves is typically composed of lead tin yellow (type II) mixed with lazurite (Figs. 7c,d); azurite was also found as a component in other areas of green. It is remarkable, although not unknown [26,27], that the expensive pigment lazurite should be used in this way, a privileging of the materials of which the artist would be aware but not necessarily either the patron or any other viewer.

As regards the blues, both lazurite and azurite are represented: the former in Fragments 1 and 5, and the latter in Fragments 2, 3, 4 and 5, typically for the larger background areas. The relatively large scale and high quality of the original volume from which Fragment 1 is derived is perhaps reflected by the use of a luminous lazurite background (Table 1) where more modest academic manuscripts would use the azurite backgrounds as found in the cuttings examined. The different colours and tones produced by the combination of lazurite with white lead is striking, though the difference between the pilgrim's mantle and James's tunic is presumably due to the predominance of azurite as the local colour of the latter, while lazurite was added to give luminous shadows to the tunic (Table 4). A remarkable feature of Fragment 5 is that Niccolò's kneeling figure has a delicate pale blue with much of the luminosity of pure lazurite, while lazurite and azurite were layered or combined to create a very different green-blue colour for St. James's tunic: the precious blue fits its wearer, but the visual result is far closer to what one would expect of an azurite-malachite blend. These pigments are all costly and therefore privileged in status wherever used in the art of this period: their presence imparts dignity to a notable degree to the individuals represented and to the manuscript which adopts them.

In Fragment 2, azurite was used with an organic red lake and other pigments to achieve a purple-brown (vermilion and carbon-based black; Fig. 7e) and a pale red (chalk). The ink in Fragment 1 has not been characterised, but is likely to be iron gall [15].

Comparison of the palettes of Fragment 1 and the Paris bible analysed by Best *et al*. [11] shows some similarities as expected, but the latter makes use of a wider palette (Table 6). On the other hand, there are significant differences between the contemporaneous Fragment 5 and the Skard manuscript [12] which may be expected from geographical considerations; the latter features orpiment, realgar, verdigris/green earth and bone white, which are absent from **5** (Table 6).

Comparison of the data with other broadly contemporaneous European illuminated manuscripts (Bensi's 2008 review [28]; see Table 6) shows there is striking similarity in the use of pigments which, furthermore, appears to extend to most of the identifications made by pXRF of the University of Glasgow Library's illuminated manuscripts [18]. But equally notable are the instances, which are few, of differences. The example of the red insect-based kermes pigment noted on one or other of the Latin manuscripts analysed [29] seems to stand alone, as does the unusual mixture of red lead and cinnabar in a Bolognese manuscript painted in a Paris workshop [30]. There may also be other instances of 'outliers' among the Glasgow manuscripts; the pinks, for example, were rendered differently: an iron, calcium and mercury-rich mixture and a lead-mercury mix in MS370 and MS6 respectively [19].

The contents of Table 6 point on the one hand to the existence of an artist's palette that had wide chronological and geographical currency. On the other, there is variability, albeit at a low level, expressing itself in the form of local adaptation or experimentation on a very local, even personal level. For instance, there appears to be as much variability *among* the five Bolognese examples as there is *between* these examples and ones executed in northern Europe in the 13th-15th C. The question then arises as to whether a more general corollary of these observations is that artists' materials and techniques were more static during this time than their styles. In any case, this issue of variability should be open to review as more analytical data become available and perhaps more significantly as more data points are taken from each manuscript. The concurrence of lazurite and azurite can be used as an example to illustrate the point: Clark's [1] finding of lazurite layered over azurite in a 13th C north Italian choir book might have appeared anomalous until Ricciardi & Delaney [31] encountered it in a work by Niccolò da Bologna, thereby apparently supporting the view that this was not uncommon at the time [32]; on the other hand, this was not found in the cutting attributed to the same painter in this study (Fragment 5), although the layer structure was not explicitly examined.

Methodologically, the high spatial resolution of RM gives it a distinct advantage over pXRF in analysing fragments such as the ones here, in which the size of many individual painted areas is small. A further advantage of RM is its ability to identify organic pigments and ones, such as the crucial lazurite, that are based on light elements; pXRF cannot detect the former and the latter only by indirect inference. pXRF systems, however, are readily portable, thereby circumventing the need to transport the object to the laboratory, coupled with the associated high insurance costs [33]. The role of pXRF is clear: it can provide a rapid preliminary and *in situ* assessment of the range of pigments and identify particular locations on the manuscript requiring subsequent more detailed (non-destructive) analysis by RM. Furthermore, the trace element content of pigments, determined by pXRF, has the potential of resolving different sources or even grades of an individual pigment (for example, Mn in a red ochre); this is a topic that could be usefully explored further.

But equally evident is that instrumentation in technical art history is constantly evolving (for example, smaller and less expensive Raman systems are more widely available), technical advances are responding to the need for finer-grained information of the kind exposed in the present study, complementarity of techniques and the availability of more refined reference collections of medieval pigments [34] will become increasingly important. As well as the role of MA-XRF [24] referred to previously, mention can be made of the developments of other techniques for examination of manuscripts used such as fiber optic reflectance spectroscopy (FORS) for point analysis of pigments [35] and binders, and the broader view of illuminations and watercolour paintings provided by hyperspectral imaging (HIS) [36-38].

Supporting data: The pXRF data are provided as supporting material (Table 7).

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Author contributions:
TDC, RJHC & RJ designed the research, TDC performed the Raman analyses; RJ carried out the p-XRF analyses; RG selected the manuscripts for study and contributed to the project's art historical aspects. All authors contributed to the writing of the article and gave final approval for publication.

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Table 1. Leviticus-Numbers manuscript - results of RM and pXRF analysis

Site #	*Colour*	*Pigment(s) identified by RM*	*Principal elements detected by pXRF*
1	Dark blue	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$)	
2	Blue/grey	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$); Lead carbonate hydroxide - lead white ($2PbCO_3.Pb(OH)_2$)	(Pb)
3	Red/orange	Lead(II,IV) oxide ($2PbO.PbO_2$)	Pb
4	Red/orange	Lead(II,IV) oxide ($2PbO.PbO_2$)	
5	Orange	Lead(II,IV) oxide ($2PbO.PbO_2$)	
6	White	Lead carbonate hydroxide - lead white ($2PbCO_3.Pb(OH)_2$)	
7	Yellow	Iron oxide ($FeOOH$); silicon dioxide (quartz, SiO_2); calcium sulphate dihydrate (gypsum, $CaSO_4.2H_2O$)	
8	Ink	-	
9	Red	Cinnabar/vermilion (HgS)	
10	Paper	-	Ca

Table 2. Tondo - results of RM and pXRF analysis

Site #	*Colour*	*Pigment(s) identified by RM*	*Principal elements detected by pXRF*
1	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Ca, Si
2	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Ca, Si
3	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	
4	Red	Vermilion (HgS)	
5	Red	Vermilion (HgS)	**Hg**, S, Ca
6	White	Lead white ($2PbCO_3.Pb(OH)_2$); vermilion (HgS)	**Pb,** Ca, S
7	White	Lead white ($2PbCO_3.Pb(OH)_2$)	
8	Black	Carbon-based black (C)	
9	Purple/brown	Azurite ($2CuCO_3.Cu(OH)_2$); vermilion (HgS); calcium carbonate (chalk,$CaCO_3$); carbon-based black (C); gypsum ($CaSO_4.2H_2O$) organic pink/red lake	**Ca**, Pb, Cu, S
10	Flesh tone	Lead white ($2PbCO_3.Pb(OH)_2$); vermilion (HgS)	
11	Flesh tone	Lead white ($2PbCO_3.Pb(OH)_2$); vermilion (HgS)	
12	Brown	Iron oxides (goethite, FeOOH/magnetite, Fe_3O_4); carbon-based black (C); vermilion (HgS); calcium carbonate (chalk, $CaCO_3$)	
13	White	Lead white ($2PbCO_3.Pb(OH)_2$)	
14	Pale red	Azurite ($2CuCO_3.Cu(OH)_2$); Calcium carbonate (chalk, $CaCO_3$); Organic pink/red lake	**Ca**, S, Al, Si, Pb, Cu
15	Yellow	Tin sulfide (mosaic gold, SnS_2)	
16	Green	Iron oxide (goethite, FeOOH)	

Table 3. Initial M cutting - results of RM and pXRF analysis

Site #	*Colour*	*Pigment(s) identified by RM*	*Principal elements detected by pXRF*
1	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Ca, Si
2	Red	Vermilion (HgS)	**Hg**, S, Cu
3	White	Lead white ($2PbCO_3.Pb(OH)_2$)	
4	Pale green	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Pb, Ca, Si
5	Yellow/brown	Calcium carbonate (chalk, $CaCO_3$)	Ca, Si, Pb
6	Pale green	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$); lead tin yellow (type II; $Pb[Sn,Si]O_3$)	
7	Pale green	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Pb, Ca, Si
8	Pale green	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$); lead tin yellow (type II; $Pb[Sn,Si]O_3$)	
9	Dark green	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$); lead tin yellow (type II; $Pb[Sn,Si]O_3$); azurite ($2CuCO_3.Cu(OH)_2$)	
10	Pale green	Azurite ($2CuCO_3.Cu(OH)_2$)	
11	Dark green	Azurite ($2CuCO_3.Cu(OH)_2$)	
12	Pale green	Lazurite ($[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$) lead tin yellow (type II; $Pb[Sn,Si]O_3$)	

Table 4. St. John the Baptist cutting - results of RM and pXRF analysis

Site #	*Colour*	*Pigment(s) identified by RM*	*Principal elements detected by pXRF*
1	Pale green	Lead white ($2PbCO_3.Pb(OH)_2$)	**Pb**, Ca
2	Dark green	Indigo	
3	White	?Calcium carbonate (chalk, $CaCO_3$)	**Ca**
4	Red	Vermilion (HgS)	**Hg**, S
5	Dark green	Azurite ($2CuCO_3.Cu(OH)_2$) Vermilion (HgS) ?iron oxide (goethite, FeOOH)	**Cu**, Pb, Ca
6	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	**Cu**, Pb, Ca, Si
7	White	Lead white ($2PbCO_3.Pb(OH)_2$)	**Pb**, Ca

Table 5. St James fragment - results of RM and pXRF analysis

Site #	*Colour*	*Pigment(s) identified by RM*	*Principal elements detected by pXRF*
1	Blue	Lazurite ([$[(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$]); lead carbonate hydroxide (*lead white*; $2PbCO_3.Pb(OH)_2$)	
2	Dark blue	Lazurite ($(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$)	
3	Blue	Azurite ($2CuCO_3.Cu(OH)_2$); lead carbonate hydroxide (*lead white*; $2PbCO_3.Pb(OH)_2$)	**Cu**, Ca
4	Blue	Azurite ($2CuCO_3.Cu(OH)_2$)	
5	Dark blue	Lazurite ($(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$)	
6	Blue	Lazurite ($(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$)	Pb, Ca
7	Black	Carbon-based black (C)	
8	Red	Vermilion (HgS)	**Hg**, S
9	Brown	Iron oxides/hydroxides (FeOOH, Fe_3O_4)	
10	White	Calcium carbonate (*chalk*; $CaCO_3$)	**Ca**, Pb
11	Flesh-tone	Vermilion (HgS); Lead carbonate hydroxide (*lead white*; $2PbCO_3.Pb(OH)_2$)	
12	Black	-	
13	Pink	Vermilion (HgS); lazurite ($(Na,Ca)_8[(Al,Si)_{12}O_{24}]S]$)	

Table 6. Comparative data

Object	*Summary results*	*Publication*
13th C Paris bible	Azurite, orpiment, lazurite, realgar, lead white, red lead, malachite and vermilion	Best *et al*. 1993 [11]
Late 14th C Ms Pal 159 Book of Hours, Paris atelier but painted by Bolognese artist	Lazurite, white lead, red cinnabar, orange lead (minium). One reddish point a red lead and cinnabar mix	Bersani *et al.* 2006 [30]
Choir books Ferrara cathedral 15th C	Lazurite, 'lacca brasile', cinnabar, azurite, minium, white lead, malachite, (massicot (PbO), marzacoto?, pararealgar)	Baraldi 2008 (RM)[39] Moioli-Seccaroni (2008) (XRF) [40]
14th C Ill. Ms (Getty Museum)	Lazurite	Schmidt *et al.* 2009 [41]
Three 15th C Latin manuscripts (MS Lat 8, MS Lat 14 and MS Lat 17)	Vermilion (HgS), kermes (kermesic acid), azurite, malachite, ivory black, white lead and lead tin yellow type (Pb_2SnO_4)	Burgio *et al.* 1997 [29]
North Italian cuttings: St Giustina of Padua by G da Cremona (c. 1470); Virgin and Child, illuminated by Franco de' Russi (2nd half 15th C); Sonnets & Triumphs by Francesco Petrarca, probably Illuminated by Bartolomeo Sanvito (1463-1464)	Lead white, gypsum, azurite, lazurite, indigo, malachite, vermilion, red lead, lead tin yellow (type I), goethite, carbon, and iron gall ink	Burgio *et al.* 2010 [15]
1. c. 1275 Paris Bible 2. 13th C north Italian antiphonal 3. 13th C north Italian Choir book	1. White lead, vermilion, red lead, lazurite, azurite and orpiment; realgar and malachite only in trace amounts 2. Mary's cloak in lazurite and mother's cloak in malachite 3. Layering lazurite over azurite	Clark 1995 [42]
Illuminated codex c. 1340	Pb white, Pb red, PbSn yellow, azurite	Bussotti *et al.* 1997 [43]
Membranous medieval codices (Fondo Vecchio 18, 9th-10th C, Messanensis S. Salv. Graec. 51, 13th C, Messanensis S. Salv. Graec. 83, 12th C)	Minium, cinnabar, lampblack, iron oxide (red ochre), PbSn yellow + lazurite, Cu compound, lazurite	Magistro *et al.* 2001 [44]
"Birth of John the Baptist" by Niccolò da Bologna (14th C)	A layer of ultramarine over azurite	Ricciardi & Delaney 2011 [31]
15th C Gutenberg Bibles	Cinnabar, lead tin yellow (type 1), carbon-based black for the ink, azurite, malachite, an organo-copper complex (a "verdigris"), calcium carbonate, gypsum, gold leaf, and lead white	Chaplin *et al.* 2005 [45]

Figure Captions:

Fig. 1 Leviticus-Numbers bible leaf, with analysis sites indicated. The fragment measures 304 mm x 225 mm and represents the so-called Bolognese ‘First Style’ (c.1250-1280?), with 2 columns of unglossed text, 190 x 135 mm; rulings at 30, 92, 104, 165, 189 mm, vertical only?).

Fig. 2 Tondo, with analysis sites indicated; c. 80 mm in diameter, painted by the so-called ‘Seneca Master’ (early 14^{th} C) showing a youthful figure holding a scroll.

Fig. 3 Large initial ‘M’ cut from a choir book, with analysis sites indicated; c.189 x 157 mm (c. 1300-1320).

Fig. 4 St. John the Baptist cutting, with analysis sites indicated; 248 x 126 mm, illuminated by the First master of Urb lat. 163 (c.1300-1330).

Fig. 5 St. James fragment, with analysis sites indicated; 120 x 70 mm, illuminated by Niccolò da Bologna (c. 1360).

Fig. 6 Raman spectra obtained for the manuscript fragments showing the spectrum for: a) vermilion (HgS), with bands at 343, 284 & 252 cm^{-1}, used for the red paints and as a component in the fleshtone and purple paints (Leviticus-Numbers manuscript, site 9; Tondo, sites 4-6 & 9-12; Initial M, site 2; St. John Baptist, sites 4-5; St James fragment, sites 8, 11 & 13); b) lead carbonate hydroxide (‘lead white’, $2PbCO_3.Pb(OH)_2$), with a characteristic strong band at 1050 cm^{-1}, found in the white paints or as a component in selected pale blue, red/fleshtone, purple and green paints (Leviticus-Numbers manuscript, sites 2 & 6; Tondo, sites 6, 7, 10, 11 & 13; Initial M, site 3; St John Baptist, sites 1 & 7; St James fragment, sites 2, 3 & 11); c) lead(II,IV) oxide (‘red lead’, $2PbO.PbO_2$), with bands at 548, 480, 390, 313, 223, 149 & 122 cm^{-1}, found only in the red-orange paint on the Leviticus-Numbers manuscript (sites 3-5); d) tin sulfide (‘mosaic gold’, SnS_2), with bands at 310 & 202 cm^{-1}, found in the yellow paint used only on Tondo (site 15); e) yellow ochre, comprising a mixture of gypsum ($CaSO_4.2H_2O$; the band at 1007 cm^{-1}), quartz (SiO_2; the band at 466 cm^{-1}) and iron hydroxides (primarily FeOOH; the bands at 680, 387 & 245 cm^{-1}), obtained for the yellow and brown paints (Leviticus-Numbers manuscript, site 7; Tondo, sites 12 & 16; St James fragment, site 9); the low signal/noise ratio in the spectrum is due to a combination of the weak scattering of the iron hydroxides and possible fluorescence from the organic binder, hence reference spectra are shown for comparison; and f) calcium carbonate ($CaCO_3$), with a characteristic strong main band at 1086 cm^{-1}, found in the white paint (Tondo, sites 9, 12 & 14; Initial M, site 5; St James fragment, site 10).

Fig. 7 Raman spectra obtained for the manuscript fragments showing the spectrum for: a) indigo, with bands at 1584, 1572, 599 & 546 cm^{-1} found in the dark green paint (St John Baptist, site 2), with the weak peaks due to the fluorescence from the organic material; b) azurite with bands at 1098, 940, 839, 403, 284, 250, 180, 138 & 86 cm^{-1}, found in the blue paints (Tondo, sites 1-3, 9 & 14; Initial M, sites 1, 4, 7 & 9-11; St John Baptist, sites 5 & 6; St James fragment, sites 3 & 4); c) a mixture of lead tin yellow (type II; $Pb[Sn,Si]O_3$), with bands at c. 330 & 136 cm^{-1} and lazurite ($[Na,Ca]_8[(Al,Si)_{12}O_{24}][S,SO_4]$), with bands at 1096, 582, 547 & 257 cm^{-1} found in the blue paints (Initial M, sites 6, 8, 9 & 12); d) lazurite ($[Na,Ca]_8[(Al,Si)_{12}O_{24}][S,SO_4]$), with bands at 1649, 1360, 1096, 803, 582, 547 & 257 cm^{-1} found in the blue paints (Leviticus-Numbers manuscript, sites 1 & 2; Initial M, sites 6, 8, 9 & 12; St James fragment, sites 1, 5, 6 & 13); and e) carbon-based black, with two characteristic broad bands at 1580 & 1360 cm^{-1} found in the black paint (Tondo, sites 8, 9 & 12; St James fragment, site 7).